

HIGH DIELECTRIC CONSTANT METAL OXIDE GATE DIELECTRICS

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Background of the Invention

Field of the Invention

15 The present invention relates generally to semiconductor structures and manufacturing. More particularly the invention relates to the formation of metal oxide gate dielectric layers for metal-oxide-semiconductor field effect transistors (MOSFETs).

20 Background

 Advances in semiconductor manufacturing technology have led to the integration of millions of circuit elements, such as transistors, on a single integrated circuit (IC). In order to integrate increasing numbers of circuit elements onto an integrated circuit it has been necessary to reduce the line
25 widths of the various parts that make up an integrated circuit. Not only have interconnect line widths become smaller, but so have the dimensions of metal-oxide-semiconductor field effect transistors.

 MOSFETs are also sometimes referred to as insulated gate field effect transistors (IGFETs). Most commonly, these devices are referred to simply as
30 FETs, and are so referred to herein.

 Transistor scaling typically involves more than just the linear reduction of the FET width and length. For example, both source/drain (S/D) junction depth and gate dielectric thickness are also typically reduced in order to produce a FET with the desired electrical characteristics. Similarly, when in use, these reduced
35 scale FETs are operated with scaled down voltages.

Over the years, a substantial amount of research and development in the field semiconductor manufacturing has been dedicated to providing reduced thickness dielectric layers, as mentioned above. However, to be suitable for use as a MOSFET gate dielectric layer, these reduced thickness dielectric layers are typically required to have certain characteristics. For example, the dielectric layer should have a low density of interface states, a low density of defects, and a dielectric breakdown voltage high enough for use with the desired voltages that the MOSFET will encounter during operation.

What is needed is a thin dielectric layer suitable for use as the gate dielectric layer in a MOSFET, and what is further needed are methods of making such a dielectric layer.

Summary of the Invention

Briefly, a method of forming a dielectric layer suitable for use as the gate dielectric layer of a MOSFET includes oxidizing the surface of a silicon substrate, forming a metal layer over the oxidized surface, and reacting the metal with the oxidized surface to form an at least partially epitaxial silicon layer superjacent the substrate, and a metal oxide layer superjacent the epitaxial silicon layer.

In a further aspect of the present invention, an integrated circuit includes a plurality of insulated gate field effect transistors, wherein various ones of the plurality of transistors have metal oxide gate dielectric layers and substantially intrinsic silicon layers subjacent the metal oxide dielectric layers.

Brief Description of the Drawings

Fig. 1 is a schematic cross-sectional view of a wafer with a first oxide layer formed on the surface thereof, a metal layer formed over the oxide layer and a capping layer formed over the metal layer.

Fig. 2 is a schematic cross-sectional view of the structure of Fig.1, after the first oxide layer is converted to a metal oxide layer and a silicon layer is formed.

Fig. 3 is a schematic cross-sectional view of the structure of Fig. 2, after the capping layer has been removed and a gate electrode has been patterned over the metal oxide layer.

Fig. 4 is a schematic cross-sectional view of the structure of Fig. 3, after
5 further processing operation to form source/drain terminals in the wafer.

Fig. 5 is a schematic cross-sectional view of a wafer with a first oxide layer formed on the surface thereof, and a metal layer formed over the first oxide layer.

Fig. 6 is a schematic cross-sectional view of the structure of Fig.5, after
10 the first oxide layer is converted to a metal oxide layer and a silicon layer is formed.

Fig. 7 is a flow diagram illustrating a process in accordance with the present invention.

Fig. 8 is a flow diagram illustrating a process in accordance with the
15 present invention.

Detailed Description

Terminology

The terms, chip, integrated circuit, monolithic device, semiconductor
20 device, and microelectronic device, are often used interchangeably in this field. The present invention is applicable to all the above as they are generally understood in the field.

Historically, the material most commonly used in the semiconductor industry to form the gate insulator layer of a FET is silicon dioxide. Thus, the
25 gate insulator layer is frequently referred to simply as the gate oxide. The expression gate dielectric is also used to describe the gate insulator layer.

The term "gate" is context sensitive and can be used in two ways when describing integrated circuits. Gate refers to a circuit for realizing an arbitrary logical function when used in the context of a logic gate. However, as used
30 herein, gate refers to the insulated gate terminal of a three terminal FET when used in the context of transistor circuit configurations or formation of transistor

structures. The expression “gate terminal” is generally interchangeable with the expression “gate electrode”. A FET can be viewed as a four terminal device when the semiconductor body is considered. However, for the purpose of describing illustrative embodiments of the present invention, the FET will be described using the traditional gate-drain-source, three terminal model.

Polycrystalline silicon is a nonporous form of silicon made up of randomly oriented crystallites or domains. Polycrystalline silicon is often formed by chemical vapor deposition from a silicon source gas or other methods and has a structure that contains large-angle grain boundaries, twin boundaries, or both. Polycrystalline silicon is often referred to in this field as polysilicon, or sometimes more simply as poly.

The expression, high dielectric constant materials, refers to materials having a higher dielectric constant than oxides of silicon. Similarly, the expression low dielectric constant materials refers to materials having a lower dielectric constant than oxides of silicon.

The letter k, is often used to refer to dielectric constant. Similarly, the terms high-k, and low-k, are used in this field to refer to high dielectric constant and low dielectric constant respectively.

Source/drain terminals refer to the terminals of a FET, between which conduction occurs under the influence of an electric field, subsequent to the inversion of the semiconductor surface under the influence of a electric field resulting from a voltage applied to the gate terminal. Generally, the source and drain terminals are fabricated such that they are geometrically symmetrical. With geometrically symmetrical source and drain terminals it is common to simply refer to these terminals as source/drain terminals, and this nomenclature is used herein. Designers often designate a particular source/drain terminal to be a “source” or a “drain” on the basis of the voltage to be applied to that terminal when the FET is operated in a circuit.

Overview

A silicon dioxide layer is reacted with an overlying metal layer to produce a silicon layer and a metal oxide layer. The metal oxide layer is suitable for use as a gate insulator layer of a MOSFET. In typical embodiments of the present invention, a silicon dioxide layer is thermally grown on the surface of a silicon substrate, and a metal layer is deposited over the silicon dioxide layer. Preferably, the metal is one that does not form a silicide. Such metals include, but are not limited to, hafnium and zirconium. The metal layer and the silicon dioxide layer are reacted to form a silicon layer and an overlying metal oxide layer. In a first embodiment of the present invention, a capping layer is formed over the metal prior to the metal being reacted with silicon dioxide. In an alternative embodiment, the metal and silicon dioxide are reacted without a capping layer over the metal.

It has long been known that electrical characteristics of MOSFETs, for example, threshold voltage, are a function of the gate insulator thickness and the dielectric constant of the gate insulator material. In the case of the threshold voltage, for example, the threshold voltage is approximately proportional to the thickness of the gate insulator layer, and further is approximately inversely proportional to the dielectric constant of the material which comprises the gate dielectric layer. From this relationship, it can be seen that a desired change in an electrical characteristic such as threshold voltage can be achieved by manipulating the thickness or the dielectric constant of the gate insulator, or both. Another way to view this is to recognize that, electrically, a thin dielectric layer having a first dielectric constant, can be equivalent to a thicker dielectric layer having a dielectric constant greater than the first dielectric constant.

The relationship between gate dielectric thickness and dielectric constant takes on particular significance in the design and fabrication of deep submicron MOSFETs. Given the dielectric constant of silicon dioxide, the traditional, and most common gate dielectric material, a thickness below about 1nm (i.e., 10 angstroms) is required for fabricating MOSFETs with desired electrical

characteristics. These extremely thin dielectric layers are difficult to fabricate and further may be sensitive to mechanical stresses, or tunneling phenomenon. However, a thicker, more robust dielectric layer, made from a material with a greater dielectric constant than that of silicon dioxide, can be used to enable
5 transistor scaling beyond (i.e., below) channel lengths of 0.1 micron.

Several high-k gate insulators, such as TiO_2 , and Ta_2O_5 , are currently formed by depositing such thin films on a silicon surface by chemical vapor deposition. However, this type of deposition operation has at least two very stringent requirements. First, that the initial silicon surface is atomically clean
10 without any native SiO_2 . This is critical to achieving equivalent SiO_2 thicknesses less than 1.0nm. Second, that the deposition and any post deposition thermal operations do not produce any SiO_2 interfacial layer. These are requirements with which it is difficult to comply.

Various illustrative embodiments of the present invention are described
15 below with reference to Figs. 1-8. Figs. 1-2 illustrate the various stages of fabrication of a metal oxide dielectric layer over an silicon layer. Portions of this silicon layer include intrinsic epitaxial silicon. Figs. 3-4 illustrate various stages of fabrication a field effect transistor having a metal oxide layer as a gate dielectric and an epitaxial silicon layer underlying the metal oxide that forms the gate
20 insulating layer. Figs. 5-6 illustrate an alternative process embodiment of the present invention wherein a metal oxide layer overlying at least one epi-Si region is formed without the use of a capping layer over the metal.

Referring now to Fig. 1, a cross-sectional view of a substrate is shown wherein a silicon substrate **102** has a shallow trench isolation structure **104**
25 disposed therein, a silicon dioxide layer **106** disposed on the surface of substrate **102**, a metal film **108** disposed over silicon dioxide layer **106**, and a capping layer **110** disposed over metal film **108**.

Shallow trench isolation structure **104** is typically filled with a dielectric material such as silicon dioxide. Those skilled in the art will recognize that

although shallow trench isolation structures are common in modern integrated circuits, such a structure is not required to practice the present invention.

Silicon dioxide layer **106** is typically formed by a thermal oxidation operation, and such operations are well known in this field. Silicon dioxide layer **106** has a thickness in the range of 5 angstroms to 100 angstroms. Those skilled in the art will appreciate that even though layer **106** is referred to as a silicon dioxide layer, such an extremely thin oxide layer may contain some number of dangling, or untied bonds, and so this layer may also more generically be referred to as an oxide of silicon. Metal film **108** is then deposited onto the surface of silicon dioxide layer **106**. Any suitable metal may be used that can be converted to a metal oxide by reaction with silicon dioxide. It is preferable that the metal selected for metal film **108** is a metal that does not react with silicon to form a silicide. It is also preferable that the metal selected for metal film **108** has a higher heat of formation than silicon dioxide. Some of the rare earth elements are suitable for use as metal film **108**. In this illustrative embodiment of the present invention, hafnium is used for metal film **108**. Zirconium is another material that can be used for metal film **108**. A typical range of thicknesses for metal film **108** is approximately 100 angstroms to 200 angstroms. A capping layer **110** is formed over metal film **108** to substantially prevent interaction of metal film **108** with the ambient environment. Capping layer **110** may be any suitable material that prevents interaction of metal film **108** with the ambient. An additional desirable characteristic of capping layer **110** is that it is substantially unreactive with metal film **108**. In the illustrative embodiment, capping layer **110** is a titanium nitride (TiN) film formed by a physical vapor deposition operation. A typical thickness for capping layer **110** is approximately 200 angstroms, but in any case capping layer **110** should be thick enough to prevent interaction of metal film **108** with the ambient environment.

Since, in this embodiment, the reaction of metal film **108** and oxide layer **106** will be limited by the amount of material in oxide layer **106**, the thickness of

metal film **108** is typically chosen such that oxide layer **106** is substantially completely converted.

In accordance with the present invention, Fig. 2 shows a schematic cross-sectional view of the structure of Fig. 1, after silicon dioxide layer **106** is converted to metal oxide layer **114** by a thermal annealing operation, typically at a temperature above approximately 600°C. This annealing operation facilitates the reaction $\text{SiO}_2 + \text{Hf} \rightarrow \text{Si(epi)} + \text{HfO}_2$. The temperature selected for the thermal annealing operation is typically chosen to be, but is not limited to, approximately one-half of the melting temperature of the metal film. The silicon produced in this reaction is substantially intrinsic and is shown in Fig. 2 as layers **112a** and **112b**. Layer **112a** represents the substantially intrinsic silicon that forms an epitaxial layer over the surface of silicon substrate **102**. Layer **112b** represents non-epitaxial silicon that may form over STI structures **104**. Alternatively, in those regions where there is an underlying STI structure, silicon formed by the reaction of the metal with the silicon dioxide may rise to the top of the metal oxide layer rather than forming underneath the metal oxide. In any case, when silicon is formed immediately overlying the STI regions, that silicon is removed so as to prevent electrical shorting between the regions separated by the STI structures. Any silicon that is formed over the STI structures is removed prior to forming a silicide over the surface of the source/drain terminals.

The re-grown epi-Si layer is substantially intrinsic. Those skilled in the art will appreciate that having an intrinsic layer immediately subjacent the gate dielectric layer may provide the additional benefit of enhanced carrier mobility in a MOSFET fabricated in this way. In one embodiment of the present invention, the silicon layer formed by the reaction of the silicon dioxide with the metal film may have a thickness in the range of about 10 angstroms to 20 angstroms.

Referring now to Fig. 3, the structure of Fig. 2 is shown after capping layer **110** is removed by etching; excess (i.e., unreacted) metal **108** is removed; and after the formation of a gate electrode **120**. Typically capping layer **110** is removed by a wet etch process. When TiN is used as capping layer **110**, sulfuric

acid or ammonium hydroxide may be used to remove the capping layer. Gate electrode **120** is disposed over metal oxide layer **114**. Conventional processing operations are used to form gate electrode **120**.

Fig. 4 shows a cross-sectional view of a MOSFET that includes patterned
5 metal oxide layer **114** as a gate insulating layer. The MOSFET also includes a gate electrode **120** disposed over metal oxide **114**, and source/drain terminals **130** disposed, substantially adjacent gate electrode **120**, as shown in Fig. 4. Those skilled in the art will recognize that many variations on this structure are possible within the scope of the present invention. For example, sidewall
10 spacers are often formed adjacent to the gate electrode of MOSFETs so as to aid in the control of source/drain terminal formation. Methods for the formation of gate electrodes, sidewall spacers, and source/drain terminals are well known in this field. Various known materials and dimensions may be selected for the gate electrodes, sidewall spacers and source/drain terminals. Typical materials
15 may include, but the present invention is not limited to, polysilicon for the gate electrode, silicon nitride for the sidewall spacers, and p-type dopants such as boron to form the source/drain terminals of p-channel MOSFETs and n-type dopants such as arsenic or phosphorous to form the source/drain terminals of n-channel MOSFETs. Similarly, well-known deposition, and patterning methods
20 may be used to form the MOSFET structure of Fig. 4.

An alternative embodiment of the present invention does not require a capping layer over the metal film, but rather requires an in-situ thermal annealing in a high vacuum. This alternative embodiment is described in conjunction with Figs. 5-6.

25 Referring now to Fig. 5, a cross-sectional view of a substrate is shown wherein a silicon substrate **102** has shallow trench isolation structures **104** disposed therein, a silicon dioxide layer **106** disposed on the surface of substrate **102**, and a metal film **108** disposed over silicon dioxide layer **106**.

Shallow trench structure **104** is typically filled with a dielectric material
30 such as silicon dioxide. Those skilled in the art will recognize that although

shallow trench isolation structures are common in modern integrated circuits, such a structure is not required to practice the present invention.

Silicon dioxide layer **106** is typically formed by a thermal oxidation operation, and such operations are well-known in this field. Silicon dioxide layer **106** has a thickness in the range of 5 angstroms to 100 angstroms. Metal film **108** is then deposited onto the surface of silicon dioxide layer **106**. Any suitable metal may be used that can be converted to a metal oxide by reaction with silicon dioxide. It is preferable that the metal selected for metal film **108** is a metal does not react with silicon to form a silicide. In this illustrative embodiment of the present invention, hafnium is used for metal film **108**. Zirconium is another material that can be used for metal film **108**. A typical range of thicknesses for metal film **108** is approximately 100 angstroms to 200 angstroms. The thickness of metal film **108** is generally chosen such that there is an adequate supply of the metal to substantially completely react with the underlying silicon dioxide layer. Typically, metal film **108** is deposited by a physical vapor deposition (PVD) process. Those skilled in the art will recognize that a PVD process is one in which a material is deposited directly from a target to a wafer, rather than being created as a reaction product and then deposited. A typical PVD process for rare earth metal deposition includes igniting a plasma formed from a gas that is inert, i.e., unreactive with the rare earth metal target, in a reaction chamber under high vacuum conditions. Argon is an example of such an inert gas. Various other PVD parameters and ranges will be apparent to those skilled in the art.

In accordance with the present invention, Fig. 6 shows a schematic cross-sectional view of the structure of Fig. 5, after silicon dioxide layer **106** is converted to metal oxide layer **114** by heating without breaking vacuum from the PVD operation. This heating operation promotes the reaction $\text{SiO}_2 + \text{Hf} \rightarrow \text{Si} + \text{HfO}_2$. In one embodiment there is a minimal, i.e., very small amount, of SiO_2 on the substrate, and the remainder of the oxygen necessary to form metal oxide layer **114** comes from an oxidizing ambient. For example, the reaction that

forms metal oxide **114** could be done in a reduced pressure chamber with partial O₂ in the ambient. Such a process would substantially preclude the possibility of unreacted SiO₂ left at the interface between the substrate and the metal oxide layer.

5 As shown in Figs. 5-6, an epi-Si layer **112a** is formed where the single crystal silicon of substrate **102** underlies silicon dioxide layer **106**. However, a silicon layer **112b** is formed over the dielectric-filled shallow trench isolation structures **104**. Silicon layer **112b** typically is not crystalline. Alternatively, silicon layer **112b** might not be formed, but rather, in the reaction between the silicon
10 dioxide and the metal film, a silicon layer may form over the metal oxide layer in those regions where there is an underlying STI region. In any case, when silicon is formed immediately overlying the STI regions, that silicon is removed so as to prevent electrical shorting between the regions separated by the STI structures. Any silicon that is formed over the STI structures is removed prior to a forming a
15 silicide over the surface of the source/drain terminals.

 The re-grown epi-Si layer **112a** is substantially intrinsic. That is, re-grown epi-Si layer **112a** is substantially free of dopant atoms. Those skilled in the art will appreciate that having an intrinsic layer immediately subjacent the gate dielectric layer may provide the additional benefit of enhanced carrier mobility in
20 a MOSFET fabricated in this way. Typically, layer **112a** is thin enough such that a MOSFET threshold voltage is substantially determined by the doping concentrations of substrate **102**.

 Once metal oxide layer **114** is formed, and excess, unreacted metal is removed, conventional processing operations may be performed so as to
25 complete a MOSFET structure as described above in connection with Figs. 3-4.

 Fig. 7 is a flow diagram illustrating a process embodying the present invention. As shown in Fig. 7, at block **202**, a layer of silicon dioxide is formed on the surface of a wafer. A metal layer is then deposited **204** over the silicon dioxide layer. Metal deposition is typically achieved by physical vapor
30 deposition. The metal is preferably one that does not form a silicide with silicon,

but one that does form a metal oxide when reacted with silicon dioxide. Hafnium and zirconium are examples of such materials that are suitable for use in forming a metal layer. The silicon dioxide and metal layer are reacted **206** to form a metal oxide layer and a silicon layer. In some embodiments, the metal may be covered by a capping layer (e.g., a TiN layer) to prevent its interaction with the reaction ambient. In other embodiments, no capping layer is used, but rather the wafer is heated without breaking the vacuum that was formed in the reaction chamber for the metal deposition operation.

Fig. 8 is a flow diagram illustrating a process embodying the present invention. As shown in Fig. 8, at block **302**, a layer of SiO_2 is grown on the surface of a silicon wafer by thermal oxidation. A metal layer is deposited **304** over the SiO_2 layer. The metal layer and the SiO_2 are reacted, generally by heating, to form **306** a silicon layer and a metal oxide layer. More particularly, the silicon layer tends to be intrinsic silicon. Furthermore, the silicon layer tends to be a crystalline silicon layer in those portions of the wafer where the SiO_2 layer was superjacent crystalline silicon of the wafer. If a capping layer was applied over the metal prior to reacting the metal with the SiO_2 , then the capping layer is removed, along with the unreacted metal, if any. A layer of material is from which a gate electrode may be patterned is then deposited **308**. The gate electrode is patterned **310**, and source/drain terminals are formed **312**. Those skilled in the art will appreciate that well-known materials and processing operations may be used to form the gate electrode and source/drain terminals, once the metal oxide layer has been formed. For example, polysilicon may be used to form the gate electrode and the source/drain terminals may be formed by implanting n-typed or p-type dopants substantially adjacent to the gate electrode. Sidewall spacers may be formed adjacent to the gate electrode prior to the formation of the source/drain terminals.

Various other layers of insulators and conducting material are formed above the gate level, as is well understood in the field of semiconductor manufacturing and integrated circuit design.

Conclusion

Embodiments of the present invention provide metal oxide dielectric layers that are suitable for use as the gate insulator layer for a MOSFET.

- 5 Methods in accordance with the present invention take advantage of the ready formation of SiO_2 on the surface of a silicon substrate, and convert the SiO_2 layer to a high-k metal oxide suitable for use as a gate dielectric layer by reacting with a thin metal film, typically, by thermal annealing.

- 10 In a further aspect of the present invention, a MOSFET is fabricated with a metal oxide dielectric. It will be recognized by those skilled in the art and having the benefit of this disclosure that the present invention is applicable to the formation of both n-channel FETs (NFETs) and p-channel FETs (PFETs).

An advantage of embodiments of the present invention is that a MOSFET gate dielectric having a higher dielectric constant than silicon dioxide is formed.

- 15 A further advantage of embodiments of the present invention is that electron mobility in a MOSFET incorporating the metal oxide dielectric is improved by providing an intrinsic layer of epitaxial silicon subjacent the metal oxide gate dielectric layer.

- 20 A further advantage of embodiments of the present invention is that the higher dielectric constant of the metal oxide dielectric layer allows a MOSFET in accordance with the present invention to have equivalent electrical performance to a MOSFET with a physically thinner silicon dioxide gate dielectric layer.

- 25 The present invention may be implemented with various changes and substitutions to the illustrated embodiments. For example, the present invention may be practiced with not only with silicon wafers as substrates, but also with other substrates, including but not limited to such substrates as silicon on insulator (SOI).

It will be readily understood by those skilled in the art and having the benefit of this disclosure, that various other changes in the details, materials, and

arrangements of the materials and steps which have been described and illustrated in order to explain the nature of this invention may be made without departing from the principles and scope of the invention as expressed in the subjoined Claims.